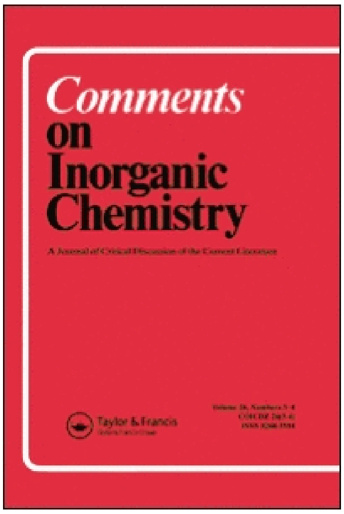

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Sm^2 in Oxide Lattices: An Unexplored Chapter of Crystal Chemistry

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Sm^{2+} In Oxide Lattices: An Unexplored Chapter Of Crystal Chemistry

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The chemistry of Sm^{2+} in solid oxide environment is reviewed and explored by a systematic search for crystal lattices stabilizing Sm^{2+} at particular reaction conditions. It is demonstrated that SrB_4O_7 is representing an unique lattice stabilizing Sm^{2+} even when crystals are prepared in air. However, when exchanging Sr by e.g. Ca, Ba, Cd, Pb, only Sm^{3+} doping could be traced. Sm^{2+} in lattices free of nuclear spins is of interest to hyperfine optical hole burning. In this respect we have prepared single crystals of $SrSO_4$ doped predominantly by Sm^{2+}. In summary, we can say that the stability of Sm^{2+} in an oxide environment is strongly depending on local effects of coordination and a reduction mechanism not revealed so far. In particular it remains unclear, why Sm^{2+} can be included into SrB_4O_7 crystals under oxidizing conditions, whereas in the rapidly cooled melt no Sm^{2+} could be traced.

Keywords: *divalent samarium; optical hole burning; oxides; crystal growth; glasses*

Abbreviations: OHB, optical hole burning, PSHB, persistent spectral hole burning, H-OHB, hyperfine optical hole burning

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INTRODUCTION

In solids some of the lanthanide ions can be present either in their divalent or trivalent state. Their electronic configurations are given by $4f^n5s^25p^6$ or $4f^{n-1}5s^25p^6$, respectively. The mostly studied divalent lanthanide species are Eu^{2+}, Sm^{2+} and Yb^{2+}.[1] Interest in divalent samarium doped materials was greatly enhanced after CaF_2:Sm^{2+} proved to be a suitable system for lasing action.[2] Single crystals of a large variety of host lattices doped with divalent samarium were grown during the years 1960–1970 in view of obtaining either laser crystals or materials suitable for fundamental optical studies.

The reduction of Ln^{3+} ions to Ln^{2+} ions in the solid state generally needs a strong reducing agent. In cases where the host-lattice was stable against a reducing atmosphere, H_2/N_2 or H_2/Ar gas mixtures have been used. However, Z. Pei et al. reported on a preparation of ceramic SrB_4O_7:Sm^{2+} without any denotable reducing agent. The solid state reaction was simply performed in air. This represents so far the only example where a valence change from Sm^{3+} to Sm^{2+} could be achieved in *air* and in an *oxide lattice*.[3] The unique observation of Z. Pei et al. rises the general question on the thermodynamic stability and on conditions for crystal lattices which may stabilize Sm^{2+}. In the present Comment we describe the solid state chemistry of Sm^{2+} as reported in literature along with our own observations. Our view may provide some guidelines for the synthesis of Sm^{2+} doped materials in the context of spectroscopy, including laser applications and particularly phenomena of *optical hole burning* (OHB).[4,5,6]

Two methods of changing the absorption properties by incident light are commonly applied. Mechanisms of *persistent* spectral hole burning (PSHP) are due to photoionization occuring in two steps. A first step involves absorption of a photon at the wavelength of the spectral hole followed by a step of photoionization.[7] Spectral holes burned by a photon gated process can be very stable, i.e. their lifetimes can extend to days, even at room temperature. This mechanism preferably occurs in glassy hosts or disordered crystals,[8,9] because of the inhomogenous line broadening involved, which allows to burn a large number of holes into a inhomogenous line. The process of *hyperfine* optical hole burning (H-OHB) can be described as follow: A given lanthanide ion is resonant with the laser frequency on only one of the allowed transitions among the hyperfine levels of both the ground and excited state, but it may relax by another allowed pathway to a different ground state level than excited. Accordingly, a depletion of this hyperfine level of the electronic ground state is reached. This type of mechanism can produce a spectral hole with the linewidth of the homogenous line. In order to gain a high memory capacity, materials of low nuclear spin moments (e.g. oxide lattices) are of interest, because in spin-rich host-lattices a broadening of the homogenous line can occur due to spin flip-flop processes (Table I). Previously, A. Caprez et al.[10] have shown, that available ions of low nuclear spin moments and suitable size for a substitution by Eu^{3+} or Pr^{3+} have the oxidation state II (Ca, Sr, Ba, Zn) or IV (Ce). This means, that host-lattices considered so far for H-OHB involve a mechanism of *heterovalent* doping, which finally turned out to be less suited.[10] Ions of the oxidation state II may, however, be substituted by *isovalent* Sm^{2+}, providing an isoelectronic configuration to Eu^{3+}. This approach opens a new perspective to the search of optimized host-lattice for hyperfine hole burning experiments in nearly spin-free materials.

EXAMPLES FEATURING LOW OXIDATION STATES OF SAMARIUM IN OXIDES

F.H. Ellinger and W.H. Zachariasen[11] reported on a phase which they believed to be SmO resulting from a heat treatment of metallic samarium. Contrary, G. Brauer et al.[12] described that the reduction of the oxyhalides (LnOX) of Nd, Sm, and Yb with LiH at temperatures between 500°C and 800°C gave neither lanthanide monoxides, nor intermediate oxides with the metallic element in a mixed valence state. This method proved successful to form EuO. However, SmO and YbO could not be obtained by oxidation of the respective metals; efforts to stabilize these monoxides in a matrix of SrO and CaO were also unsuccessful. The redox couple Eu^{3+}/Eu^{2+} features the highest oxidation ability in aqueous solution under standard conditions (-0.35V) among the lanthanides, followed by Yb^{3+}/Yb^{2+} (-1.15V) and Sm^{3+}/Sm^{2+} (1.56V).[13]

M. Gasgnier and P. Caro[14] rejected a recent claim by B.M.S. Bist et al.[15] saying, that gadolinium and samarium monoxide thin films have been observed. Moreover, experimental and theoretical evidences[16] are available to demonstrate that the lanthanide monoxide “LnO” generally cannot be prepared in the solid state except of EuO and possibly YbO. This behaviour is confirmed by the standard Gibbs energy change ΔG° for the reaction $Ln + Ln_2O_3 \rightarrow 3Ln^{2+}O^{2-}$ derived from ionization potentials. These thermodynamic considerations show that the divalent lanthanide monoxides should be unstable. However, exceptions are known for EuO ($\Delta G° = -141$ kJ), YbO ($\Delta G° \sim 0$ kJ). The $\Delta G°$ value for the formation of SmO was calculated to be +142 kJ.[17] To the best of our knowledge, the most recent article about obtaining SmO was published by C.N. Christodoulou and T. Takeshita in 1992:[18] Formation of a f.c.c. SmO apart b.c.c. Sm_2O_3 was reached by a heat treatment of Sm metal under argon flow or in vacuum. All this various results summarized above describe the difficulties in obtaining Sm(II) in an *oxide* environment.

DIVALENT SAMARIUM IN OXIDE GLASSES

Since PSHB was first observed for Sm^{2+} ions at room temperature, glasses doped with Sm^{2+} ions have attracted much attention for a possible application in high-density memory devices. Glasses doped with Sm^{2+} ions, are considered more favourable for high-density optical memories than crystals, because of a wide spectral inhomogeneous width, high transparency and amenability to mass production.[19]

Although Sm^{3+} was found to be quite stable in fluoride glasses, Sm^{2+}-doped glassy states were nevertheless obtained. Glasses were prepared by melting procedures subject to a strongly reducing atmosphere. However, fluorescence spectroscopy showed that some Sm^{3+} remained.[20,21]

Along a sol-gel process Al_2O_3-SiO_2:Sm^{3+} oxide glasses were prepared from an alkoxy-derived solution by M. Nogami et al.[22] The Sm^{2+} ions were introduced in the glass matrix by heating the Sm^{3+} in H_2 gas atmosphere. Aluminum oxide was used because this helped to change the valence state of the samarium ions in glasses.[23] The porous glasses allowed for a diffusion of H_2 molecules reducing the Sm^{3+} ions within a short reaction period at moderately low temperatures (800°C). The reaction of Sm^{3+} with H_2 was described by a first-order kinetic and involved the formation of H_2O:

$$2Sm^{3+} + O^{2-} + H_2 \rightarrow 2Sm^{2+} + H_2O\ ,^{19}$$

where O^{2-} surrounding the Sm^{3+} being also bound to Si^{4+} or Al^{3+} ions. The fluorescence intensity of the Sm^{2+} ions was increased for reactions at a high temperature, and a maximum value was reached when heated to ~800°C. Above 900°C, the fluorescence intensity of Sm^{2+} started to decrease. These results suggest that on the one hand the kinetic is responsible for the reduction of trivalent samarium, but on the other hand the *local structure surrounding the samarium* has also a considerable effect on the stability of the divalent state. Glasses treated as described started to precipitate mullite crystals above ~900°C. The crystallisation of mullite decreases the Al_2O_3 content, which may shift the redox potential in favour of the trivalent samarium.[19]

Similarly, in some borate glasses, Sm^{3+} could be reduced to Sm^{2+}. K. Hirao et al.[24] produced a glass by B_2O_3, Na_2CO_3, and Sm_2O_3 in a glassy carbon crucible under a reducing atmosphere. Such glasses were containing both divalent and trivalent samarium. Other borate glasses were prepared which included Al_2O_3.[25,26]

LOW OXIDATION STATES OF SAMARIUM IN HALIDE CRYSTALS

The alkaline earth fluorides MF_2 (M = Ca, Sr, Ba) first received particular attention, SmF_3 being the doping agent in this case.[27] MF_2:Sm^{2+} single crystals were grown in vacuo according to the Bridgman method in graphite or molybdenum crucibles. Graphite powder or metal fillings were added to the batch to create reducing conditions.[28,29] The Czochralski and the zone melting techniques applied in inert gas atmosphere were also used. An extensive survey of the optical spectra of divalent lanthanide ions in calcium fluoride was presented by D.S. McClure and Z. Kiss[30]. Another possibility used apart from a chemical reduction was the preparation of Ln^{2+} by γ-irradiation of CaF_2 crystals.

Later on, additional compounds showing other structures than the fluorite structure have been investigated. These comprise the alkaline-earth halides MX_2 and halogenofluorides MXF (M = Ca, Sr, Ba; X = Cl, Br)[31,32,33,34], the perovskites ABF_3 (A = Na, K, Rb; B = Ca, Mg)[32,35], and the alkali halides MX (M = Na, K, Rb; X = Cl, Br, I).[36,37,38,39] With respect to the perovskites, it was not possible to dope $KCaF_3$ crystals with divalent samarium due to a suitable Ca site for Sm^{3+}.[40]

Single crystals of all these compounds were grown according to methods similar to those used in the case of the MF_2 hosts; the lanthanide impurity was introduced as a samarium salt adapted to the matrix. Purified hydrogen was often acting as the reducing agent. L.L. Chase et al.[41] have obtained the absorption and emission spectra for the Sm^{2+} in the mixed fluorides $Ca_{1-x}Y_xF_{2+x}$ and $Ca_{1-x}La_xF_{2+x}$. Mixed crystals of the PbFCl-type family featuring a composition of $Sr_yBa_{1-y}FCl_xBr_{1-x}$ have been investigated by H. Bill et al.[8,9,42,43,44,45] Selected examples discussed above do not claim to be a complete list of investigation. However, it should be representative.

TABLE I Naturale abundance and magnetic moments of the most frequent isotopes with non-vanishing nuclear spin. Elements showing less than 20% of a total abundance of isotopes with non-vanishing spin are margined by bold types

Element	*Natural abundance of the most frequent isotopes with non-vanishing nuclear spin in %*	*Magnetic moments in magnetic magnetons μ_N of the most frequent isotopes*	*Natural abundance of additional isotopes with non-vanishing nuclear spin in %*	*Magnetic moments in magnetic magnetons μ_N of additional isotopes*
B	80.1	2.69	19.9	1.8
Ba	**11.2**	**0.94**	**6.6**	**0.84**
Br	50.7	2.11	49.3	2.27
C	**1.1**	**0.70**		
Ca	**0.1**	**-1.32**		
Cd	12.8	–0.59	2.2	–0.62
Cl	75.8	0.82	24.2	0.68
F	100	2.63		
Mg	**10.0**	**-0.86**		
O	**0.04**	**-1.89**		
Pb	22.1	0.59		
S	**0.8**	**0.64**		
Si	**4.7**	**-0.56**		
Sr	**7.0**	**-1.09**		
W	**14.3**	**0.12**		
Zn	**4.1**	**0.88**		

Only three lanthanides have divalent states which were so far accessible in organometallic compounds: Eu, Yb and Sm. However, the Sm(II) chemistry appeared to be the most difficult one.[46] The oxidation ability under standard conditions for the redox couple Ln^{3+}/Ln^{2+} indicates that Eu^{2+} should be the most stable among these ions, whereas Sm^{2+} is the most reactive in terms of reducing power.

Of considerable interest for the lanthanide-organic chemistry was the discovery of the decamethylsamarocen(II) 1a and its thf adduct 1b:[47,48]

$$\mathbf{1a} \quad (\eta^5 - C_5Me_5)_2Sm$$

$$\mathbf{1b} \quad (\eta^5 - C_5Me_5)_2Sm(thf)_2 \quad .$$

The most common precursor for Sm-organic compounds is $SmI_2(thf)_x$, one of the only Sm(II) chemicals, which is commercially available. Due to the existence of SmI_2, we guess that *soft π-bases are stabilizing the divalent state* of *samarium*. In contrast to Sm(II), the trivalent samarium which is considered a hard π-acid may be stabilized by the hard π-bases such as O^{2-}. The remarkable chemical behaviour of divalent samarium in organometallic compounds was described by assuming that samarium(II) has a radical like nature,[49] although, this can not be explained on the basis of its f^6 electronic configuration. The two complexes la and lb are generally known as reducing agents due to the strong one electron reducing capacity of the Sm(II) center.[50]

THE ANALYSIS OF PARTICULAR OXIDE CRYSTAL LATTICES AND GLASSES

Spectroscopy

To determine the valance state of the samarium ions incorporated in a number of compounds discussed below, fluorescence spectra were traced in the range from 550 nm to 800 nm using a xenon 367 nm excitation wavelength, which is suitable for the excitation of both Sm^{2+} and Sm^{3+}. Broad bands observed around 17500 cm^{-1} (571 nm), 16500 cm^{-1} (606 nm) and 15300 cm^{-1} (654 nm), can be attributed to the ${}^4G_{5/2} \rightarrow {}^6H_{5/2,\,7/2,\,9/2}$ transitions of the Sm^{3+} ion, respectively. Relatively sharp fluorescence lines are observed at about 14640 cm^{-1} (683 nm), 14300 cm^{-1} (699 nm), 13790 cm^{-1} (725 nm), which are attributed to the $^5D_0 \rightarrow ^7F_{0,\ 1,\ 2}$ transitions of the Sm^{2+} ion.[22] The fluorescence lines in our measurements can differ from this values due to the different host lattices. All spectra were measured with a SPEX Fluoromax™ Spectrofluorometer at 300K.

Silicates

Silicates and tungstates seem to be suitable for H-OHB with respect to the nuclear spin density (Table I). Hardystonite ($Ca_2ZnSi_2O_7$) belongs to the silicate minerals, called melilites. $Ca_2ZnSi_2O_7$ crystallizes in the tetragonal space group $P\bar{4}2_1m$. The structure can be described by sheets of $[ZnSi_2O_7]^{4-}$. Adjacent sheets are held together by Ca^{2+} ions, showing a coordination number of 8. The site symmetry of Ca^{2+} being substituted by samarium is C_s.[51] Previous doping experiments showed that this lattice can not be doped effectively by trivalent lanthanides.[52] At a concentration of 2 mol% in the melt (with respect to Ca^{2+}) saturation is already reached in the solid state at a level of 0.04 mol%. We assume that the charge compensation mechanism for a heterovalent substitution of Ca^{2+} by Pr^{3+} or Sm^{3+} is not very effective. However, this behaviour could have been used as a mechanism to enter divalent samarium into crystals. This because, the isovalent substitution of Ca^{2+} by Sm^{2+} should be more likely than introducing Sm^{3+}. This is clearly contradicted by the fluorescence spectra of $Ca_2ZnSi_2O_7$:Sm measured at 300K, which showed no hint of the existence of divalent samarium. Enforcement by using carbon led to a decomposition of the melt, because of the reduction of ZnO to Zn^0. However, the 8-fold Ca^{2+}-site provides a radius of 112 Å to which Sm^{3+} (1.079 Å; CN:8) may fit closer than Sm^{2+} (1.27 Å; CN:8).

Because of (i) the reduction of ZnO and (ii) a more suitable size given by the Sr^{2+}-site (1.26 Å; CN:8), we have replaced Zn^{2+}, Ca^{2+} by Mg^{2+}, Sr^{2+} ions, correspondingly. This leads to the compound strontio-akermanite ($Sr_2MgSi_2O_7$), featuring the same structure as hardystonite.[53] In this case MgO is more stable against a reduction than ZnO. During crystal growth an excess of MgO and SiO_2 was used to suppress the formation of the merwenite phase, $Sr_3MgSi_2O_8$.[54] Transparent crystals of optical quality were obtained, but Figure 1 indicates only the existence of trivalent samarium also for this host lattice.

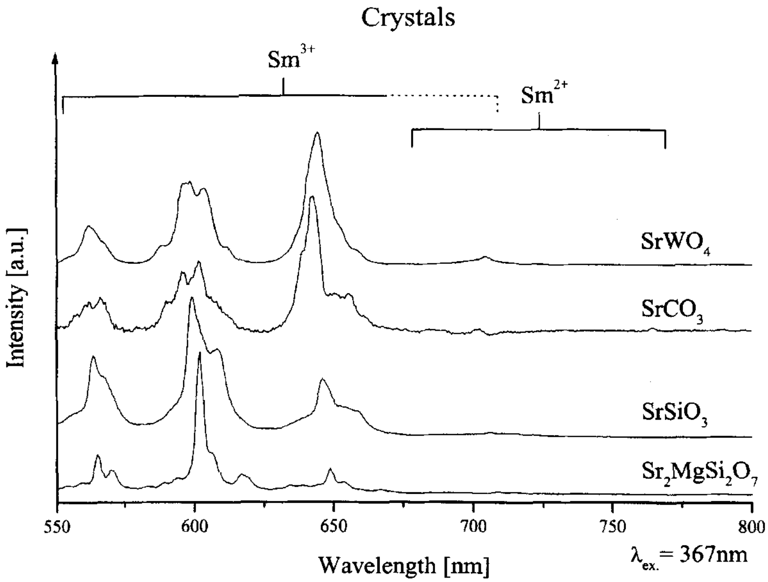

FIGURE 1 Fluorescence spectra of $SrWO_4$, $SrCO_3$, $SrSiO_3$, $Sr_2MgSi_2O_7$ crystals doped with Sm

For $Sr_2MgSi_2O_7$ the following charge compensation mechanisms are proposed:[52]

i. $Sm_2O_3 + 3Sr_{Sr} \rightarrow 3SrO + 2Sm^{+}_{Sr} + V^{2-}_{Sr}$, which leads to one Sr^{2+} vacancy;

ii. $Sm_2O_3 + MgO + 2Sr_{Sr} + Si_{Si} \rightarrow 2SrO + SiO_2 + 2Sm^{+}_{Sr} + Mg^{2-}_{Si}$, which leads to a Mg^{2+} on a Si^{4+} site.

In order to avoid a predominant charge compensation mechanism following reaction (ii), another silicate ($SrSiO_3$) was tested. In this case a substitution of Si^{4+} by Sr^{2+} is not likely, due to the different sizes of corresponding sites. We attempted to growth $SrSiO_3$:Sm by Czochralski method under an Ar/H_2 atmosphere, despite $SrSiO_3$ undergoes a phase transition. Again, we have obtained crystals containing only trivalent samarium (Figure 1)!

In all these experiments we used Sm^0 and Sm_2O_3 for the preparation of a possible intermediate monoxide by reduction of the sesquioxide with the pure metal:

$$\mathrm{Sm}^{3+}(\mathrm{sol.}) + \mathrm{Sm}^0 \rightleftharpoons \mathrm{Sm}^{2+}(\mathrm{sol.}).$$

The formation of small amounts of divalent samarium was expected to appear in the melt at temperatures slightly above the melting point of the host lattice under an Ar- or Ar/H_2- (90:10 mol%) flow of 20 ml/min. Sm_2O_3 and Sm were mixed and pressed into a tablet pressured at 10 tons/cm^2. Such pellets were filled into a crucible and covered with the prereacted starting material. In cases where we did not proceed in this way, most of the metallic Sm (m.p. 1074°C, b.p. 1794°C) evaporated just during heating the charge.

Tungstates

In previous experiments, $CaWO_4$ was grown by the Czochralski method.[10] For doping attempts, Eu_2O_3 was added to the melt. Under Ar/O_2 (99:1 mol%) the melt should preferably stabilize Eu^{3+},[55] but in the crystal almost all Eu appeared in the divalent state!

In experiments using $SrWO_4$ (isostructural to $CaWO_4$) and Sm_2O_3, we could trace only Sm^{3+} (Figure 1). Trivalent samarium was obtained, even when using Sm metal as starting material under an atmosphere of Ar/H_2 (90:10 mol%). In this case, black crystals resulted due to the reduction of the tungstate ion.

Borates: MB_4O_7 (M = Ca, Sr, Ba, Cd, Pb)

Ceramic samples of $SrB_4O_7{:}Sm^{2+}$ were prepared by solid state reactions in air. Stoichiometric amounts of $SrCO_3$, H_3BO_3 including 1 mol% excess of H_3BO_3 to compensate for the B_2O_3 evaporation, were mixed and ground. The mixtures were heated at 700°C in either a corundum, porcelain or platinum crucible for 5 hours to effect CO_2 removal. A second annealing step was necessary at 850°C in order to accomplish the reactions. At this state 0.5 mol% Sm_2O_3 was added and the mixtures were heated a third time up to 850°C for another 5 hours.[3] All steps

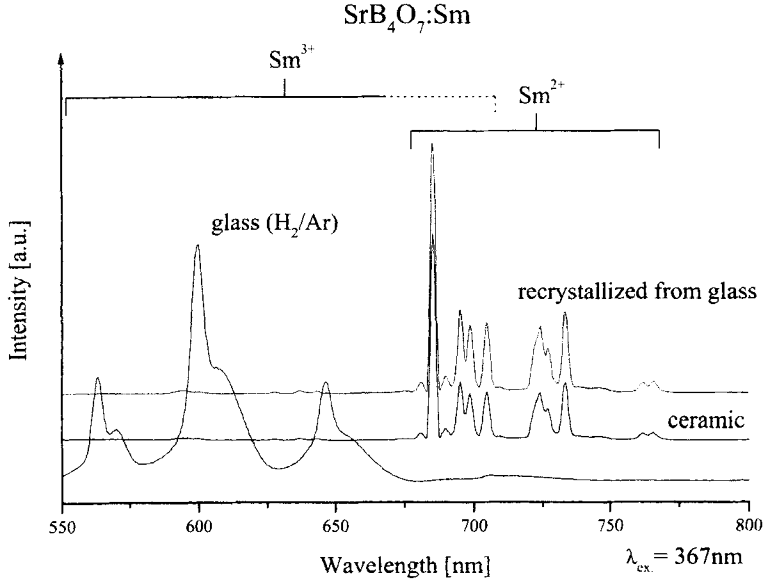

FIGURE 2 Fluorescence spectra of: (i) $SrB_4O_7:Sm^{2+}$ annealed at 850°C in air, (ii) $SrB_4O_7:Sm^{2+}$ after melting at 1050°C for 30 min. in H_2/Ar, and (iii) recrystallized from the glassy state at 850°C during 48 hours

were carried out in air. Following this procedure, the flourescence spectrum of crystalline SrB_4O_7:Sm (Figure 2) showed the emission lines of Sm^{2+}. Glasses were prepared from crystalline $SrB_4O_7:Sm^{2+}$, in the way as described above: the material was melted at 1080°C in air, Ar or H_2/Ar. The melt was kept at this temperature for 30 min., followed by cooling. All the glasses produced under different atmospheres were showing only the emission lines of *trivalent* samarium (Figure 2). The valance change from divalent to trivalent samarium obviously took place during the phase change *into the crystalline state.* In the liquid phase only the trivalent state seems to be stable. Surprising to notice, that a glass made by melting materials under a H_2 atmosphere using Sm_2O_3 featured *mostly trivalent* samarium.[56] However, recrystallization of this borate-glass in *air* at 850°C induced a valence change to the *divalent* state (Figure 2).

Crystal growth of SrB_4O_7:Sm was performed using the Czochralski method[57] under *air.* Knowing that in the glassy phase only Sm^{3+} was present (Figures 3, 4), to our surprise, the crystals growing from the melt contained predominantly Sm^{2+}.!

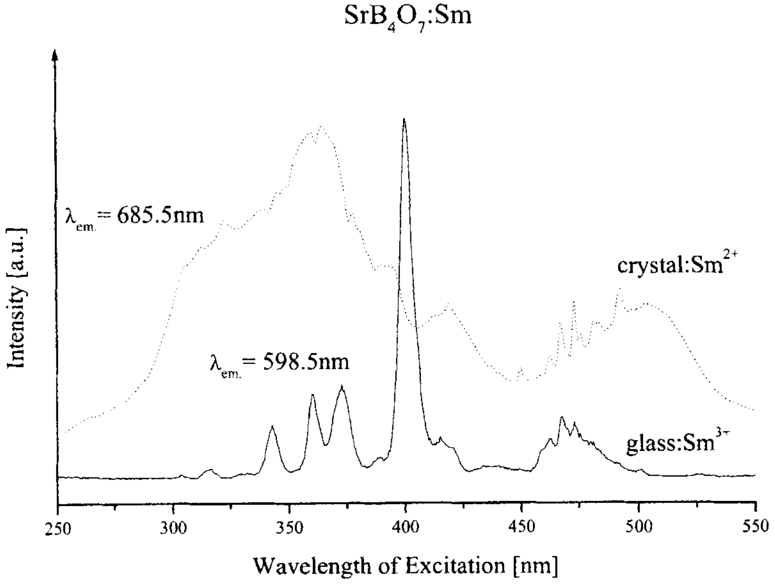

FIGURE 3 Excitation spectra of: (i) Sm^{3+} in a glassy matrix of SrB_4O_7, and (ii) Sm^{2+} in a crystalline matrix of SrB_4O_7 with $\lambda_{em.}$ = 598.5 nm for $Sm^{3+}$and $\lambda_{em.}$ = 685.5 nm for Sm^{2+}, respectively

SrB_4O_7 crystallizes in the orthorhombic system, $P2_1nm$. The crystal structure consists of an unusual type of borate framework, which is assumed to be responsible for the reduction process from Sm^{3+} to Sm^{2+}.[3] This compound was reported to be the first example of an anhydrous borate featuring only tedrahedrally coordinated boron in which all the boron and oxygen atoms are involved in the borate network. Although the tetrahedra form a three-demensional network by corner sharing, the borate network gives the appearance of a layer-like structure because there are comparatively few links in the c-direction. The layers can be described in terms of chains (parallel to a) of six-membered rings having B-O edges in common. Furthermore, the network generates channels parallel the b-axis. The Sr ions fit into these channels. Another unusual structural feature is the occurrence of an oxygen

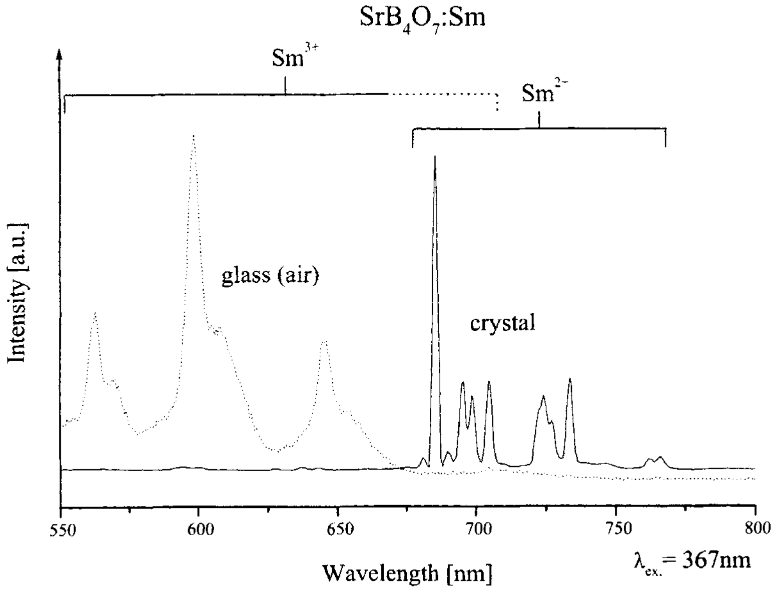

FIGURE 4 Fluorescence spectra of Sm either in glassy or single crystalline SrB_4O_7

atom coordinated to ***three boron*** atoms. These triple coordinated oxygen atoms are located in the second coordination sphere of the Sr atom at a distance of 3.04 to 3.2 Å. There are nine nearest-neighbour oxygen atoms (Figure 5), surrounding Sr^{2+} at irregular distances ranging from 2.52 to 2.82 Å (C_s site symmetry).[58]

Based on phenomenona concerning the reduction process of trivalent to divalent samarium in strontium tetraborate (air-atmosphere), we have tried to reproduce this behaviour when using other members of the tetraborate-composition: MB_4O_7 (M = Ca, Ba, Cd, Pb). *Lead* tetraborate is isostructural to strontium tetraborate.[58] To form PbB_4O_7, the temperature of the annealing process had to be changed; because of the lower melting point of PbB_4O_7 when compared to SrB_4O_7. In this case the second and third annealing steps were carried out at 700°C. In order to compare this product to SrB_4O_7, we also have annealed SrB_4O_7 at 700°C. The emission spectra of SrB_4O_7:Sm after annealing at 700°C or 850°C differ only in the intensity ratio of Sm^{2+} with respect to Sm^{3+} (Figure 6).

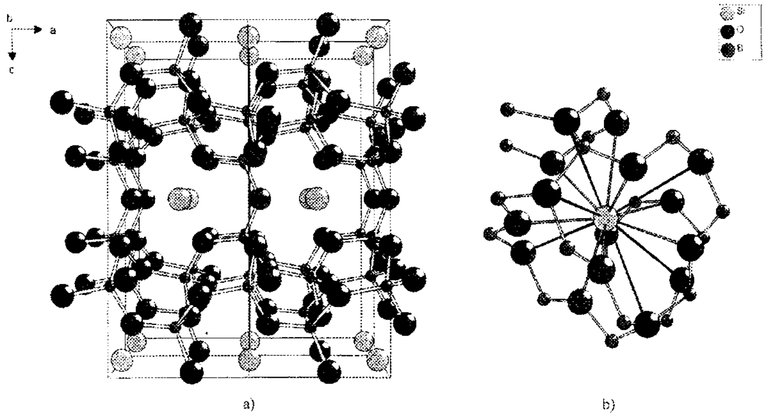

FIGURE 5 a) Structure of SrB_4O_7 showing the boron-oxygen network. b) First and second coordination sphere of the Sr^{2+} site in SrB_4O_7. Black bonds are drawn from Sr to oxygen atoms of the second coordination sphere, grey lines correspond to bonds to the oxygen within the first coordinations sphere, respectively. Note that the oxygens of the second coordination sphere (dark) are coordinated to *three* boron atoms

The same procedure used for the synthesis of SrB_4O_7:Sm was applied to form the compounds *Ca*B_4O_7:Sm (space group $P2_1/n$)[59], *Cd*B_4O_7:Sm (space group Pbca)[60] and *Ba*B_4O_7:Sm (space group $P2_1/c$),[61] respectively. Figure 6 shows the fluorescence spectra of the MB_4O_7:Sm (M = Ca, Sr, Ba, Cd, Pb) series: in the case of the Ca-, Ba-, Cd-, Pb-tetraborate compounds the lines of Sm^{3+} are dominating the spectra. There is no evidence for detectable *divalent* samarium, even not by using an excitation of 367 nm. In contrast, the *strontium* tetraborate annealed at 700°C or 850°C clearly shows the characteristic emissions peaks of Sm^{2+} ions. However, there are still emission lines of residual Sm^{3+} ions preferably seen at the 403 nm excitation.

These experiments on ceramic products support *an unique stabilization of* Sm^{2+} *in the lattice of* SrB_4O_7. All other compounds of the same empirical formula MB_4O_7 indicate no valence change of the trivalent samarium when similar conditions are applied as in the synthesis of SrB_4O_7. This is rather amazing with respect to PbB_4O_7, because this compound shows the same crystal structure as strontium tetraborate. The size of the Pb^{2+} site (1.35 Å; CN: 9) should almost be as suitable as

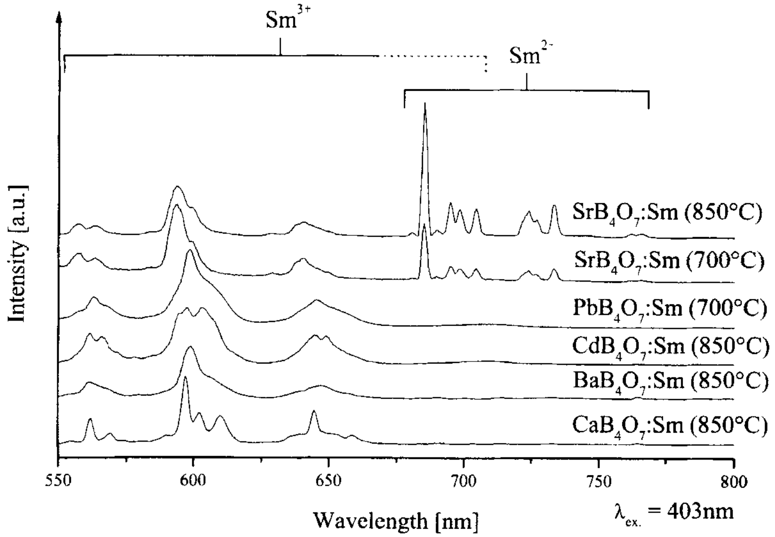

FIGURE 6 Fluorescence spectrum of ceramic samples of $CaB_4O_7:Sm^{3+}$, $BaB_4O_7:Sm^{3+}$, $PbB_4O_7:Sm^{3+}$, $CdB_4O_7:Sm^{3+}$, $SrB_4O_7:Sm^{3+/2+}$ (annealing temperatures are given in brackets)

the one of the Sr^{2+} site (1.31 Å; CN: 9) for a subsitution by Sm^{2+} (1.32 Å; CN: 9), except the effect of the lone pair of Pb^{2+}.

Evidence for a valence change from trivalent to divalent samarium may not appear along the series MB_4O_7 (M = Ca, Ba, Cd), because of the size of the $M^{2+} \neq Sr^{2+}$. Other aspects may be related to the *local coordination polyhedron* and further details of the structure, which are described in literature as followed: Strontium tetraborate shows a completely different type of network than other borates, having all the boron atoms in fourfold coordination. As a consequence, some of the oxygen atoms are coordinated by *three* boron atoms.[60] Finally, we come to conclude that we are still far off understanding the unique Sm^{2+} occurence in SrB_4O_7.

Sulfates

$SrSO_4:Sm^{2+}$ would represent a suitable system for H-OHB investigations due to the low nuclear spin density of the atoms involved (Table I). $SrSO_4$ belongs to the orthorhombic space group Pbnm with $Z = 4$.[62] Crystal growth out of the melt is not possible due to the decomposition of the compound before melting. Crystal growth by a flux method is more likely in order to avoid decomposition of SO_4^{2-}. We used LiCl as a flux to dissolve $SrSO_4$.[63,64] 17mol% $SrSO_4$ powder was mixed with 83 mol% LiCl powder, placed in a glassy carbon crucible. 2 mol% samarium (with respect to the Sr^{2+} concentration) were added as $SmCl_3$ or $SmI_2(thf)_x$. $SrSO_4$ seeds were introduced to facilitate nucleation. The charge was heated up to ~ 600°C in an Ar/H_2 (80:20 mol%) flow of 10ml/min. Crystallization was carried out at a cooling rate of 0.2°C/h down to a temperature of 4°C below the eutectic temperature (524°C).[65] Thereafter, the rate was increased to 60°C/h down to room temperature. The solvent could be removed by hot water. Finally, crystals of the size about 4 × 4 × 4 mm featuring optical quality were recovered. The fluorescence spectra (Figure 7) shows unambigously that trivalent and divalent samarium are coexistent. The total level of doping, determined by inductively coupled plasma optical emission spectroscopy (ICP-OES), however, is quite low (between 0.003 and 0.02 mol% Sm). At a lower content of H_2 in Ar/H_2 of 5–10 mol%, spectra demonstrate, that predominantly Sm^{2+} can be incorporated into $SrSO_4$ (Figure 7). This demonstrates the sensibility of the system to yield conditions allowing to trap only Sm^{2+}.

Contrary to our present procedure, there is an electrochemical approach to obtain $SmSO_4$, being isostructural to $SrSO_4$. L.B. Asprey et al. have synthesized powder samples by this method.[66]

In case of isostructural compounds such as $SrSO_4$ and $SmSO_4$ solid solution formation should allow to dope $SrSO_4$ with Sm by higher amounts than found in our experiments. There are three explanations given here for the low doping concentrations: i) In the flux there is only a small amount of divalent samarium available, the residue is in the trivalent state, (ii) the solid solution is not stable at our relatively low tem-

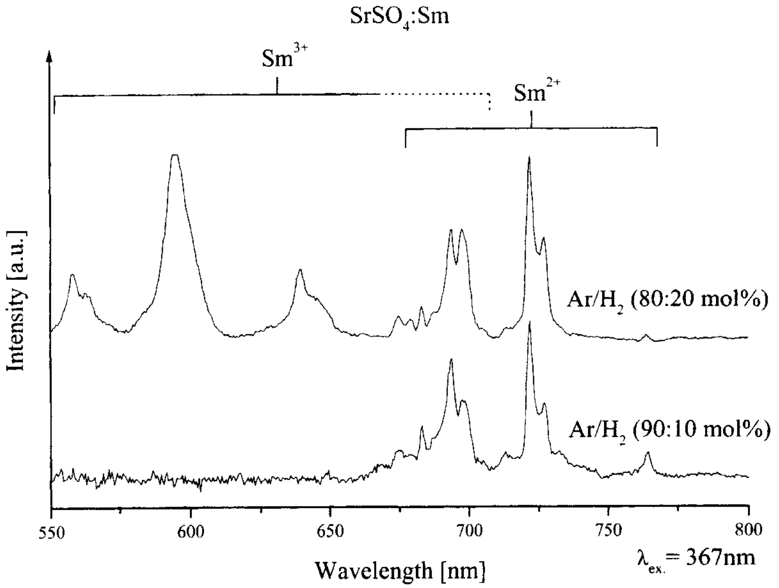

FIGURE 7 Fluorescence spectrum of $SrSO_4$ doped with Sm^{2+} and Sm^{3+}; crystallized from a flux under an (i) Ar/H_2 (90:10 mol%) or (ii) Ar/H_2 (80:20 mol%) atmosphere

perature of growth, $SmSO_4$ may only be stable under the conditions chosen in the electrochemical approach, or (iii) the solvent is strongly influencing the distribution coefficient.

Alternative methods yielding Sm^{2+} doped sulfate crystals used X- or γ-irradiation: In this way Sm^{3+} could be reduced to Sm^{2+}, leaving a hole trapped in the $CaSO_4$ lattice.[67,68] Additionally, $BaSO_4:Sm^{2+}$ [69] and $Sr_{1-x}Ba_xSO_4:Sm^{2+}$ [70] materials have been produced by a γ-irradiation exposure of a Co^{60}γ-source. These materials were investigated for *persistent* spectral hole burning properties.

Carbonates

The nuclear spin density of all elements, constituing the lattice of $SrCO_3$ are suitable for H-OHB. Following the procedure applied to the growth of $SrSO_4$ we have attempted to dope $SrCO_3$ by Sm^{2+}. The flux consisted of Li_2CO_3.[71] An atmosphere of 1-2 bar (at 800°C) CO_2 was chosen, in order to suppress the decomposition of CO_3^{2-} to CO_2. 43 mol% $SrCO_3$ and 57 mol% Li_2CO_3 were mixed together with 3mol% $SmI_2(thf)_x$ and heated up to 820°C. From there the system was cooled down to 640°C at a rate of 2°C/h, and later on at a rate of 60°C/h down to room temperature. To our great surprise, the fluorescence spectrum of Sm-doped $SrCO_3$ showed no evidence for Sm^{2+}; only lines of Sm^{3+} could be traced (Figure 1)! Obviously, conditions applied in the reduction using C, CO_2 and CO did not efficiently stabilize Sm^{2+} in the nutrient or in the lattice.

CONCLUSIONS

It is undoubtly an intersting question as to why Sm^{3+} can quantitatively change the valance state to Sm^{2+} in *air* at high temperature in *only one compound* (SrB_4O_7), whereas in other materials it turned out to be almost impossible even when using strong reducing agents. As a result of our broad search and experimental attempts, we may now draw a few conclusions in order to provide some understanding of the Sm^{2+} chemistry in oxide lattices:

- In order to avoid preferred incorporation of Sm^{3+}, the host lattice should only provide M^{2+} sites of an appropriate size fitting to Sm^{2+}. These are generally applied criteria including *charge* and *size*.
- As demonstrated by a few examples reported in organometallic chemistry as well as given by existing SmX_2 (Cl^-, Br^-, F^-) compounds, it seems that *soft-bases* can stabilize the divalent state of Sm. In this respect, O^{2-} may act as a hard ligand, yielding stability for $Sm^{2+}(O^{2-})_n$ only in case of a *particular geometry of the coordination sphere*. The unique appearence of Sm^{2+} in SrB_4O_7 seemingly documents the particular role of the influence of an O^{2-} rich environment. When Sr was exchanged by Pb or others, giving rise to a small or larger structural change, no significant Sm^{2+} incorporation could be achieved.

  That the local geometry is of crucial importance, is furthermore supported by the growth of SrB_4O_7 from the melt: In the melt and solidified glass no Sm^{2+} could be detected at 300K.

- Because of the particular occurence of Sm^{2+} in SrB_4O_7, Hartree-Fock calculations of the site energy would be of great interest, in order to compare the stability to distortions (Pb-compound) of this structure type and other geometries of the local coordination sphere as set up by Ca-, Ba-, Cd-tetraborates.
- The case of using $SrSO_4$ and Sm^{3+} as starting materials including proper reduction conditions (Figure 7) demonstrates, that in some additional cases, it may be possible to prepare Sm^{2+} in an *oxide lattice.* With respect to H-OHB, $SrSO_4$:Sm^{2+}may represent a particularly interesting system subject to further optical investigations.
- Along our analysis it remains still not clear, why Z. Pei et al. (confirmed by our own and repeated experiments) succeded in preparing SrB_4O_7:Sm^{2+} in air, when using Sm_2O_3 and *no further reductive components.*

The examples given with respect to the Sm^{3+}/Sm^{2+} equilibrium demonstrate that the chemistry of some Ln^{n+} ($n \neq 3$) systems can strongly depend on the ligand field and the reaction conditions applied during materials synthesis.

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Note added in proof: Recent experimental investigation led to the conclusion, that the Sm^{3+} to Sm^{2+} reduction in air and at high temperature may be associated with a formation of superoxide or peroxide ions (P. Mikhail et al.). Mean-while, optical hole burning in Sm^{2+} doped SrB_4O_7 and $Sr_2MgSi_2O_7$ crystals has been achieved (H. Bill et al.).

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